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MRS Workshop Explores the Diversity of 3D Multifunctional Ceramic Composites

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The MRS Workshop on Three-Dimensional Multifunctional Ceramic Composites was held at the Beckman Institute on the campus of the University of Illinois at Urbana-Champaign (UIUC) October 3–5, 2005. Organized by **Paul V. Braun** of UIUC, **C. Jeffrey Brinker** of the University of New Mexico and Sandia National Laboratories, and **Shanhui Fan** of Stanford University, the workshop reached an audience of about 100 attendees from academic institutions, government laboratories, and private industry. The scientific and technical underpinnings of self-assembly and properties of self-assembled 3D ceramic, composite, and semiconductor structures were emphasized. The technical program consisted of invited presentations from renowned experts, along with selected contributed presentations, posters, and hands-on tutorials given by expert faculty. The topics explored included new developments in 3D photonic crystals, chemical and biological sensors, nanoparticle assemblies, rapid fabrication techniques, active membranes, 3D holographic patterning, and modeling and theory of 3D optical devices.

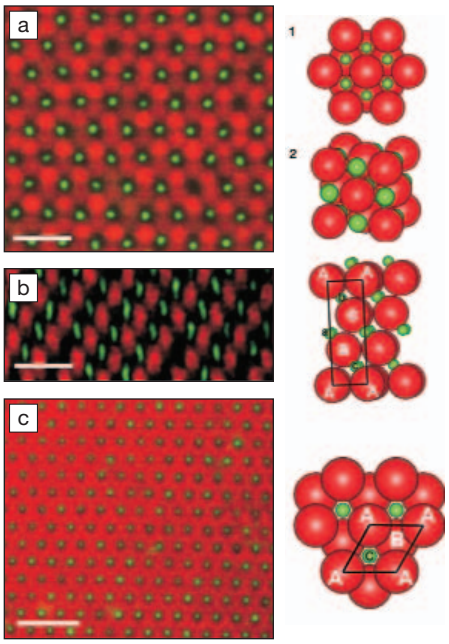

Figure 1. Laser scanning confocal microscope images of binary colloidal crystals formed from charged (red, radius 1.16 μm) and uncharged (green, radius 0.36 μm) poly(methyl methacrylate) (PMMA) particles in an index-matching solvent. (a), (b) NaCl-type crystals. (a) NaCl-type crystal with a hexagonal plane and the unit cell in a hexagonal (1) and a cubic (2) representation. (b) NaCl-type crystal with a plane perpendicular to the hexagonal close-packed layers, showing the ABC-stacking of both the large and small particles. (c) NiAs-type crystal with a superposition of confocal images of 10 layers, and the corresponding model. All scale bars are 8 μm. Reprinted by permission from Nature ***437*** *(2005) p. 235.*

J.A. Rogers (UIUC) opened the workshop with his presentation on the phase mask holographic formation of 3D polymer and inorganic–organic composite microstructures. In this work, he demonstrated that complex 3D microstructures can be formed over large areas in photoresist using only a simple contact phase mask formed from poly(dimethylsiloxane) (PDMS) and fairly incoherent ultraviolet light. This lecture was the first in a number of presentations by speakers demonstrating the formation of photonically active 3D microstructures by self-assembly and directed assembly routes. D. O'Brien (Army Research Laboratory) presented his work on creating large-area photonic crystals through both interferometric lithography and colloidal assembly. Although the defect density in these crystals is higher than for colloidal crystals formed through more complex routes, he noted that good colloidal crystals could be formed through simple spin-coating techniques. In another route to ordered 3D microstructures, he demonstrated the modern 3D microscale example of the bubble raft model.

Formation and characterization of complex 3D micro- and nanostructures were investigated by a number of the presenters. For example, D. Pine (New York University) demonstrated the construction of complex colloidal assemblies through surface-tension-driven aggregation. The resulting colloidal "molecules" have, for example, triangular, tetrahedral, and octahedral symmetries. Pine then explored several routes to combine these colloidal molecules into larger colloidal crystals that may exhibit unique optical properties. As it is well known that fcc colloidal crystals are not ideal for photonic applications, the tetrahedral clusters Pine has created may provide a needed route to colloidal crystals with diamond symmetries. Complex colloidal structures can also be formed through the assembly of mixtures of different-sized building blocks. A. van Blaaderen (Utrecht University) and C. Murray (IBM) each showed their routes to creating complex binary colloidal crystals. Van Blaaderen forms his structures from mixtures of micron-sized particles (see Figure 1), while Murray creates binary colloidal crystals from dispersions of inorganic nanoparticles. In both cases, complex structures with unique electrical and optical properties were formed. Although work remains to fully understand the properties and assembly of these binary crystals, these studies suggest that through accurate control of particle size and charge, it should be possible to self-assemble polymer, ceramic, semiconductor, and metal building blocks into metamaterials with all the same symmetries seen in ionic or metallic solids.

Workshop co-organizers Jeff Brinker (left) of Sandia National Laboratories and Paul Braun of the University of Illinois at Urbana-Champaign enjoy the evening reception at the MRS Workshop on Three-Dimensional Multifunctional Ceramic Composites. Workshop co-organizer Shanhui Fan of Stanford University is not pictured.

One powerful route to the assembly of 3D multifunctional composite structures is the biologically mediated synthesis and assembly of materials. Several presentations on this topic demonstrated that biological macromolecules found in living organisms can be used to direct the formation of composite structures with unique properties. Y. Lu (UIUC) presented his work on using enzymatically active DNA to direct the formation of nanoparticle assemblies, and for the removal of errors from such self-assembled structures. This work is unique, as it represents a new

route to correction of the errors inherent in self-organized media. Along a similar line, J.E. Hutchison (University of Oregon) showed a number of detailed projects where DNA was used to assemble nanoparticles into complex 1D and 2D structures. Biological macromolecules were also demonstrated to be active for directing the mineralization of inorganic materials. R.R. Naik (Air Force Research Laboratory) showed how polypeptide sequences could drive the deposition of silica even under very mild conditions. B.F. Chmelka (University of California, Santa Barbara) presented a number of nuclear magnetic resonance (NMR) and other characterization experiments which provided a deep understanding of the structure of the inorganic pore walls in mesoporous materials formed by a number of routes, both synthetic and biological.

The hands-on tutorials preceding the technical sessions were a unique and important part of this workshop. There have been a number of recent developments in the formation, properties, and modeling of 3D ceramics and composites that are best explored in a hands-on environment. Laboratories on the campus of UIUC were used for a number of the tutorials. The following six tutorials were given by experts in their respective fields: Opal Synthesis, Assembly, and Characterization (Instructor: P.V. Braun); Introduction to Photonic Crystals (Instructor: S. Fan); 3D Holographic Lithography (Instructor: P. Wiltzius, UIUC); Direct-Write Assembly of 3D Structures (Instructor: J.A. Lewis, UIUC); Self-Assembly of Porous and Composite Nanostructures (Instructor: C.J. Brinker); and DNA-Based Assembly and Sensing (Instructor: Y. Lu, UIUC). The tutorials included theory and optical characterization of photonic crystals, the principles and practice of holographic lithography, the fundamentals of ink-based direct-write assembly, self-assembly of highly ordered inorganic and organic mesoporous materials, and the design, synthesis, and characterization of DNA for assembly and sensing of a broad range of analytes.

Margaret Shyr and Florencio García-Santamaría, both of UIUC, discuss Shyr's research at the poster session.

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PAUL BRAUN
Chair and Co-Organizer